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(54) Title: FUNGICIDAL 1,2,4-OXADIAZOLES AND ANALOGUES		
(57) Abstract		
<p>Compounds of formula (I), where W is H or halogen, and R is alkyl or trifluoromethyl and compounds of formula (II), where X is O or S; Y is alkyl, cycloalkyl, cycloalkenyl, alkenyl or alkynyl, each of which is optionally substituted, hydrogen or acyl; R¹ is a phenyl or a 5- or 6-membered heterocyclyl group, each of which is optionally substituted; R² and R³ are hydrogen or alkyl or together with the nitrogen to which they are attached can form an optionally substituted ring which can contain 0 to 3 extra hetero atoms selected from nitrogen, oxygen or sulfur; and R⁴ is hydrogen or acyl; have activity as fungicides.</p> <div style="display: flex; justify-content: space-around; align-items: center;"> <div data-bbox="768 1144 1242 1386"> <p style="text-align: right;">(I)</p> </div> <div data-bbox="768 1449 1128 1680"> <p style="text-align: right;">(II)</p> </div> </div>		

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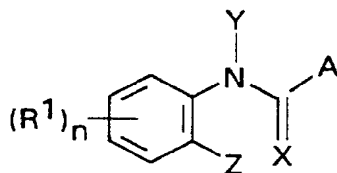
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FUNGICIDAL 1,2,4-OXADIAZOLES AND ANALOGUES

5 This invention relates to compounds having fungicidal activity.

In WO 95/25723, we have claimed compounds of formula



where

10 X is O or S;

A is a 6 membered heteroaryl group comprising at least one nitrogen atom, which is optionally substituted by one or more of the group R²;

15 R¹ is alkyl, cycloalkyl, cycloalkenyl, alkenyl, alkynyl, or amino, (each of which is optionally substituted), Y¹-X-, halogen, cyano, nitro, acyl, acyloxy, optionally substituted heterocyclyl or optionally substituted phenyl; or two adjacent groups together with the carbon atoms to which they are attached can form an optionally substituted benzo ring;

20 R² has the same meaning as R¹ or two adjacent groups together with the carbon atoms to which they are attached can form an optionally substituted heterocyclic ring;

Y is alkyl, cycloalkyl, cycloalkenyl, alkenyl or alkynyl, each of which is optionally substituted, hydrogen or acyl;

Y¹ has the same meaning as Y or is optionally substituted phenyl or optionally substituted heterocyclyl;

25 Z is C(=X¹)-X²-R³, cyano, nitro, amino, acyl, optionally substituted heterocyclyl, -C(R⁵)=N-OR⁶ or -C(R⁵)=N-NR⁶R⁷;

R³ is alkyl, cycloalkyl, cycloalkenyl, alkenyl, alkynyl, phenyl or heterocyclyl, each of which is optionally substituted, hydrogen or an inorganic or organic cationic group;

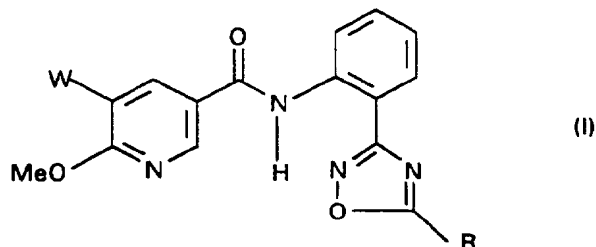
30 X¹ and X², which may be the same or different, are O or S;

R^5 , R^6 and R^7 , which may be the same or different, are alkyl, cycloalkyl, cycloalkenyl, alkenyl, alkynyl, phenyl or heterocyclyl, each of which is optionally substituted or hydrogen or R^6 and R^7 together with the atom(s) to which they are attached can form a ring;

5 and n is 0 to 4, as fungicides.

We have now found that a selected group of compounds where Z is an oxadiazole group have particularly valuable properties.

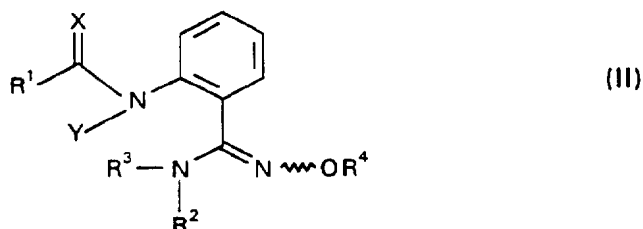
10 Accordingly, in one aspect the invention provides the compounds of formula I:



where W is H or halogen, and R is alkyl or trifluoromethyl, and complexes thereof.

The closest compound in WO 95/25723 is No 177, which is a compound where Z is 5-methyl-1,3,4-thiadiazol-2-yl and A is 6-methoxy-3-pyridyl. In the compounds of the present invention, not only is the sulfur of the thiadiazole replaced by oxygen but the oxadiazole of the present invention is attached to the phenyl from the 3-position compared with the 2-position in the prior art compound. Also in the prior art diazole ring, the nitrogens are adjacent to each other whereas they are separated by a carbon in the oxadiazole of the invention. We have also found that the oxadiazole analogue of the present invention has improved activity compared with said prior art compound.

We have also found that intermediates to the compounds of formula I and their analogues have fungicidal activity and accordingly the invention provides compounds of formula II



where

X is O or S;

Y is alkyl, cycloalkyl, cycloalkenyl, alkenyl or alkynyl, each of which is optionally substituted, hydrogen or acyl;

5 R¹ is a phenyl or a 5 or 6 membered heterocyclyl group, each of which is optionally substituted

R² and R³ are hydrogen or alkyl or together with the nitrogen to which they are attached can form an optionally substituted ring which can contain 0 to 3 extra hetero atoms selected from nitrogen, oxygen or sulfur; and

10 R⁴ is hydrogen or acyl;

together with complexes with metal salts, as well as salts with bases of compounds which are acids and salts with acids of compounds which are bases.

In the compounds of formula I, R is preferably an alkyl group of 1 to 6, especially 1 to 15 4 carbon atoms, and preferably methyl.

W is preferably hydrogen or chlorine and especially hydrogen.

A particularly preferred specific compound is 6-methoxy-2'-(5-methyl-1,2,4-oxadiazol-20 3-yl)nicotinamide.

In the compounds of formula II

Optional substituents on R¹ are alkyl, cycloalkyl, cycloalkenyl, alkenyl, alkynyl, or amino, (each of which is optionally substituted), Y¹-X-, halogen, cyano, nitro, 25 acyl, optionally substituted heterocyclyl or optionally substituted phenyl; or two adjacent groups together with the carbon atoms to which they are attached can form an optionally substituted benzo or heterocyclic ring.

Y¹ has the same meaning as Y or is optionally substituted phenyl or optionally 30 substituted heterocyclyl.

Alkyl groups are preferably of 1 to 20, e.g. 1 to 6, carbon atoms. Alkenyl and alkynyl groups are generally of 3 to 6 carbon atoms. Cycloalkyl or cycloalkenyl groups are preferably of 3 to 8 carbon atoms.

Substituents, when present on any alkyl, cycloalkyl, cycloalkenyl, alkenyl or alkynyl moiety include halogen, azido, cyano, optionally substituted alkoxy, optionally substituted alkylthio, hydroxy, nitro, optionally substituted amino, acyl, acyloxy, optionally substituted phenyl, optionally substituted heterocyclyl, optionally substituted phenoxy and optionally substituted heterocycloxy. Cycloalkyl or cycloalkenyl groups may also be substituted by alkyl.

Substituents when present on any phenyl or heterocyclyl group are usually one or more of the same groups as defined for R¹.

10

The term heterocyclyl includes both aromatic and non-aromatic heterocyclyl groups. Heterocyclyl groups are generally 5, 6 or 7-membered rings containing up to 4 hetero atoms selected from nitrogen, oxygen and sulfur. Examples of heterocyclyl groups are furyl, thienyl, pyrrolyl, pyrrolinyl, pyrrolidinyl, imidazolyl, dioxolanyl, oxazolyl, thiazolyl, imidazolyl, imidazoliny, imidazolidinyl, pyrazolyl, pyrazolinyl, pyrazolidinyl, isoxazolyl, isothiazolyl, oxadiazolyl, triazolyl, thiadiazolyl, pyranlyl, pyridyl, piperidinyl, dioxanyl, morpholino, dithianyl, thiomorpholino, pyridazinyl, pyrimidinyl, pyrazinyl, piperazinyl, triazinyl, thiazolinyl, benzimidazolyl, tetrazolyl, benzoxazolyl, imidazopyridinyl, 1,3-benzoxazinyl, 1,3-benzothiazinyl, oxazolopyridinyl, benzofuranyl, quinolinyl, quinazolinyl, quinoxalinyl, sulfolanyl, dihydroquinazolinyl, benzothiazolyl, phthalimido, benzofuranyl, azepinyl, oxazepinyl, thiazepinyl, diazepinyl and benzodiazepinyl.

20

Amino groups may be substituted for example by one or two optionally substituted alkyl or acyl, or two substituents can form a ring, preferably a 5 to 7-membered ring, which may be substituted and may contain other heteroatoms, for example morpholine, thiomorpholine, or piperidine. When R² and R³ form a ring it is generally also a 5 to 7 membered ring. These rings can be substituted as for heterocyclyl.

30

The term acyl includes the residue of sulfur and phosphorus-containing acids as well as carboxylic acids. Examples of acyl groups are thus -COR⁵, -COOR⁵, -CXNR⁵R⁶, -CON(R⁵)OR⁶, -COONR⁵R⁶, -CON(R⁵)NR⁶R⁷, -COSR⁵, -CSSR⁵, -S(O)_pR⁵, -S(O)₂OR⁵, -S(O)_pNR⁵R⁶, -P(=X)(OR⁵)(OR⁶), -CO-COOR⁵, where R⁵,

R⁶ and R⁷ are as defined previously, or R⁶ and R⁷ together with the atom(s) to which they are attached can form a ring, p is 1 or 2 and X is O or S.

Complexes are usually formed from a salt of formula MAn₂, in which M is a divalent metal cation, e.g. copper, manganese, cobalt, nickel, iron or zinc and An is an anion, e.g. chloride, nitrate or sulfate.

The invention also includes tautomers of compounds of formula II, where one or both of R² and R³ is hydrogen.

10

In the compounds of formula II:

X is preferably O;

Y, R² and R³ are preferably hydrogen;

R¹ is preferably phenyl or pyridyl, preferably substituted by one or two groups selected from halogen, especially chlorine, and methoxy, or by methylenedioxy; and

15

R⁴ is preferably hydrogen, acetyl, propionyl or methoxyacetyl.

The compounds of the invention have activity against other pathogens of Deuteromycete, Ascomycete, Phycomycete and Basidiomycete origin, especially against fungal diseases of plants, e.g. mildews and particularly cereal powdery mildew (*Erysiphe graminis*), cucumber powdery mildew (*Erysiphe cichoracearum*), vine downy mildew (*Plasmopara viticola*) and vine powdery mildew (*Uncinula necator*), rice blast (*Pyricularia oryzae*), cereal eyespot (*Pseudocercospora herpotrichoides*), rice sheath blight (*Pellicularia sasakii*), grey mould (*Botrytis cinerea*), wheat brown rust (*Puccinia recondita*), late tomato or potato blight (*Phytophthora infestans*), apple scab (*Venturia inaequalis*) and glume blotch (*Leptosphaeria nodorum*). Some compounds may be active against only a few pathogens whereas others may have a broader spectrum of activity.

25

30

The compounds of the invention have particularly advantageous activity against fungal pathogens of plants and particularly those pathogens of Ascomycete origin, especially against mildew diseases of plants, particularly cereal powdery mildew (*Erysiphe graminis*), cucumber powdery mildew (*Erysiphe cichoracearum*), vine downy mildew

(*Uncinula necator*), and apple powdery mildew (*Podosphaera leucotricha*). However some compounds may be active against other pathogens of Deuteromycete, Ascomycete, Phycomycete and Basidiomycete origin, e.g. rice blast (*Pyricularia oryzae*), cereal eyespot (*Pseudocercospora herpotrichoides*), rice sheath blight
5 (*Pellicularia sasakii*), grey mould (*Botrytis cinerea*), wheat brown rust (*Puccinia recondita*), late tomato or potato blight (*Phytophthora infestans*), apple scab (*Venturia inaequalis*) and glume blotch (*Leptosphaeria nodorum*). Some compounds may be active against only a few pathogens whereas others may have a broader spectrum of activity.

10

The compounds of the invention are generally formulated in conventional compositions used for fungicides. These compositions can contain one or more additional pesticides, for example compounds known to possess herbicidal, fungicidal, insecticidal, acaricidal or nematocidal properties.

15

The diluent or carrier in the composition of the invention can be a solid or a liquid optionally in association with a surface-active agent, for example a dispersing agent, emulsifying agent or wetting agent. Suitable surface-active agents include anionic compounds such as a carboxylate, for example a metal carboxylate of a
20 long chain fatty acid; an N-acylsarcosinate; mono- or di-esters of phosphoric acid with fatty alcohol ethoxylates or salts of such esters; fatty alcohol sulfates such as sodium dodecyl sulfate, sodium octadecyl sulfate or sodium cetyl sulfate; ethoxylated fatty alcohol sulfates; ethoxylated alkylphenol sulfates; lignin sulfonates; petroleum sulfonates; alkyl-aryl sulfonates such as alkyl-benzene
25 sulfonates or lower alkylnaphthalene sulfonates, e.g. butyl-naphthalene sulfonate; salts of sulfonated naphthalene-formaldehyde condensates; salts of sulfonated phenol-formaldehyde condensates; or more complex sulfonates such as the amide sulfonates, e.g. the sulfonated condensation product of oleic acid and N-methyl taurine or the dialkyl sulfosuccinates, e.g. the sodium sulfonate of dioctyl
30 succinate. Nonionic agents include condensation products of fatty acid esters, fatty alcohols, fatty acid amides or fatty-alkyl- or alkenyl-substituted phenols with ethylene oxide, fatty esters of polyhydric alcohol ethers, e.g. sorbitan fatty acid esters, condensation products of such esters with ethylene oxide, e.g. polyoxyethylene sorbitan fatty acid esters, block copolymers of ethylene oxide and
35 propylene oxide, acetylenic glycols such as 2,4,7,9-tetramethyl-5-decyne-4,7-diol,

or ethoxylated acetylenic glycols. Examples of a cationic surface-active agent include, for instance, an aliphatic mono-, di-, or polyamine as an acetate, naphthenate or oleate; an oxygen-containing amine such as an amine oxide or polyoxyethylene alkylamine; an amide-linked amine prepared by the condensation
5 of a carboxylic acid with a di- or polyamine; or a quaternary ammonium salt.

The compositions of the invention can take any form known in the art for the formulation of agrochemicals, for example, a solution, a dispersion, an aqueous emulsion, a dusting powder, a seed dressing, a fumigant, a smoke, a dispersible
10 powder, an emulsifiable concentrate or granules. Moreover it can be in a suitable form for direct application or as a concentrate or primary composition which requires dilution with a suitable quantity of water or other diluent before application.

15 As a dispersion, the composition comprises a compound of the invention dispersed in a liquid medium, preferably water. It is often convenient to supply the consumer with a primary composition which can be diluted with water to form a dispersion having the desired concentration. The primary composition can be provided in any one of the following forms. It can be a dispersible solution which
20 comprises a compound of the invention dissolved in a water-miscible solvent with the addition of a dispersing agent. A further alternative comprises a compound of the invention in the form of a finely ground powder in association with a dispersing agent and intimately mixed with water to give a paste or cream which can if desired be added to an emulsion of oil in water to give a dispersion of active
25 ingredient in an aqueous oil emulsion.

An emulsifiable concentrate comprises a compound of the invention dissolved in a water-immiscible solvent together with an emulsifying agent and which is formed into an emulsion on mixing with water.

30

A dusting powder comprises a compound of the invention intimately mixed with a solid pulverulent diluent, for example, kaolin.

A granular solid comprises a compound of the invention associated with similar
35 diluents to those which may be employed in dusting powders, but the mixture is

granulated by known methods. Alternatively it comprises the active ingredient adsorbed or absorbed on a pre-granular diluent, for example, Fuller's earth, attapulgite or limestone grit.

- 5 A wettable powder usually comprises the active ingredient in admixture with a suitable surfactant and an inert powder diluent such as china clay.

Another suitable concentrate, particularly when the product is a solid, is a flowable suspension concentrate which is formed by grinding the compound with
10 water, a wetting agent and a suspending agent.

The concentration of the active ingredient in the composition of the present invention is preferably within the range of 1 to 30 per cent by weight, especially 5 to 30 per cent by weight. In a primary composition the amount of active
15 ingredient can vary widely and can be, for example, from 5 to 95 per cent by weight of the composition.

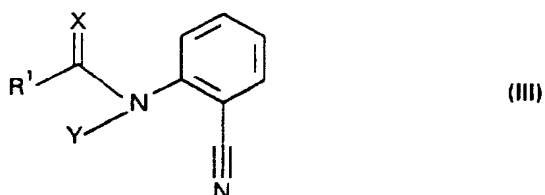
The compound compounds are generally applied to seeds, plants or their habitat. Thus, the compound can be applied directly to the soil before, at or after drilling
20 so that the presence of active compound in the soil can control the growth of fungi which may attack seeds. When the soil is treated directly the active compound can be applied in any manner which allows it to be intimately mixed with the soil such as by spraying, by broadcasting a solid form of granules, or by applying the active ingredient at the same time as drilling by inserting it in the
25 same drill as the seeds. A suitable application rate is within the range of from 5 to 1000 g per hectare, more preferably from 10 to 500 g per hectare.

Alternatively the active compound can be applied directly to the plant by, for example, spraying or dusting either at the time when the fungus has begun to
30 appear on the plant or before the appearance of fungus as a protective measure. In both such cases the preferred mode of application is by foliar spraying. It is generally important to obtain good control of fungi in the early stages of plant growth as this is the time when the plant can be most severely damaged. The spray or dust can conveniently contain a pre- or post-emergence herbicide if this is
35 thought necessary. Sometimes, it is practicable to treat the roots of a plant

before or during planting, for example, by dipping the roots in a suitable liquid or solid composition. When the active compound is applied directly to the plant a suitable rate of application is from 0.025 to 5 kg per hectare, preferably from 0.05 to 1 kg per hectare.

5

The compounds of formula II may be prepared in known manner, for example by reacting a compound of formula III

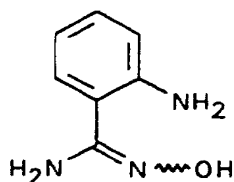


with a hydroxylamine salt, preferably hydroxylamine hydrochloride, to give a compound where R², R³ and R⁴ are hydrogen.

The R groups can be modified in known manner. For instance the compound can be reacted with a compound, R⁴Q, where Q is a leaving group such as halogen.

15 Compounds of formula III are either known or can be prepared in known manner (e.g. as described in our WO 95/25723).

Alternatively anthranilamide oxime



20 can be reacted with a compound



where Q is as defined above to give a compound of formula II where X is oxygen, and Y is hydrogen and R⁴ is -COR¹.

25 If desired compounds can be modified in known manner to give other compounds where X and/or Y have other desired values, and if desired modifying compounds

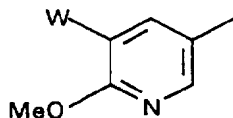
of formula I in known manner to give compounds where the R groups have other values.

Thio groups may be oxidised using a suitable oxidising agent, e.g. m-chloro-perbenzoic acid, to give sulfinyl and sulfonyl groups.

5

Compounds where X is O can be converted to compounds where X is S by sulfurising the carbonyl group in known manner, e.g. using Lawesson's reagent or phosphorus pentasulfide.

- 10 Compounds of formula I may be prepared from the corresponding compound of formula II where X is O; R³, R⁴, R⁵ and Y are hydrogen and R¹ is



- where W is as previously defined, by heating with an acylating agent, e.g. an acid anhydride of formula (RCO)₂O, where R is as previously defined, to give the desired compound.
- 15

The invention is illustrated in the following Examples. Structures of isolated novel compounds were confirmed by nmr and/or other appropriate analyses.

20

Example 1

- A mixture of N-(2-cyanophenyl)-6-methoxynicotinamide (31 g), hydroxylamine hydrochloride (17 g), potassium carbonate (17 g), water (250 ml) and methanol (250 ml) was heated under reflux for 24 hours. The mixture was cooled to room temperature, diluted with water and extracted with ether. The extract was dried and evaporated under reduced pressure to give N-{2-[amino(hydroxyimino)methyl]-phenyl}-6-methoxynicotinamide, m.p. 162-4° C (Compound 1a)
- 25

- In similar manner N-(2-cyanophenyl)-4-fluorobenzamide gave N-{2-[amino(hydroxyimino)methyl]phenyl}-4-fluorobenzamide, m.p. 190-1° C (Compound 1b)
- 30

Example 2

A mixture of compound 1a (28.6 g) in dry tetrahydrofuran (500 ml) was treated with acetic anhydride (100 ml). The mixture was stirred and heated slowly to reflux. It was then heated under reflux for 2 hours, cooled to room temperature and evaporated under reduced pressure. The residue was added to water (1 l), stirred for one hour at room temperature. Ethyl acetate was added and the insoluble white solid was collected and dried to give N-{2-[amino(acetoxymino)-methyl]phenyl}-6-methoxynicotinamide, m.p. 177-80° C (Compound 2).

10 Example 3

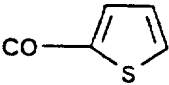
A solution of acetyl chloride (0.14 g) in dry tetrahydrofuran (2 ml) was added dropwise over 10 minutes to a stirred solution of compound 1b (0.5 g) in dry tetrahydrofuran (20 ml) having cooled to a temperature of 0-5° C. The mixture was stirred for 48 hours at room temperature. It was then evaporated under reduced pressure and the residue was partitioned between water and dichloromethane. The aqueous layer was extracted twice more with dichloromethane and the combined organic extracts were washed with brine, dried and evaporated under reduced pressure. The residue was re-crystallised from toluene to give N-{2-[amino(acetoxymino)methyl]phenyl}-4-fluorobenzamide, m.p. 182-4° C (Compound 3a).

In a similar manner, anthranilamide oxime was treated with 3,4-dimethoxybenzoyl chloride to give N-{2-[amino(3,4-dimethoxybenzoyloxyimino)methyl]phenyl}-3,4-dimethoxybenzamide, m.p. 183-183.5° C (Compound 3b).

Example 4

In a similar manner to one of the processes disclosed in the previous Examples, the following compounds of formula II where X is O and Y, R² and R³ are H, were obtained:

5

Compound	R ¹	R ⁴	m.p.(° C)
4	5-Cl-6-MeO-3-pyridyl	benzoyl	188-90
5	5-Cl-6-MeO-3-pyridyl	propionyl	127-8
6	5-Br-2-furyl	H	156-8
7	3,4-OCH ₂ CH ₂ O-phenyl	propionyl	156-8
8	3,4-(MeO) ₂ -phenyl	H	198-200
9	3,4-(MeO) ₂ -phenyl	propionyl	off-white solid
10	3,4-(MeO) ₂ -phenyl	acetyl	148-50
11	6-MeO-3-pyridyl	COCH ₂ OMe	160-1
12	6-MeO-3-pyridyl	propionyl	173-4
13	3,4-OCH ₂ O-phenyl	H	187-8
14	3,4-OCH ₂ O-phenyl	acetyl	206-7
15	3,4-(MeO) ₂ -phenyl	COBu ^t	156-62
16	3,4-(MeO) ₂ -phenyl	CO- 	169-72
17	3,4-(MeO) ₂ -phenyl	COPri	138-41
18	3,4-(MeO) ₂ -phenyl	COCH ₂ Bu ^t	163-8
19	3,4-(MeO) ₂ -phenyl	COcyclohexyl	145-55
20	3,4-(MeO) ₂ -phenyl	COPr	150-5
21	3,4-(MeO) ₂ -phenyl	COBu ⁱ	139-44

Compound	R ¹	R ⁴	m.p.(° C)
22	3,4-(MeO) ₂ -phenyl	CObenzyl	119-30
23	3,4-(MeO) ₂ -phenyl	COcyclopropyl	152-9
24	3,4-(MeO) ₂ -phenyl	COCH ₂ OMe	122-6
25	3,4-(MeO) ₂ -phenyl	COCH = C(Me) ₂	137-45
26	3,4-(MeO) ₂ -phenyl	COpentyl	128-9
27	2-CF ₃ -phenyl	acetyl	167-8
28	2-Me-phenyl	acetyl	155-6
29	4-Ph-phenyl	acetyl	186-7
30	4-Bu ^t -phenyl	acetyl	172-3
31	1-naphthyl	acetyl	142-3
32	3-Cl-phenyl	acetyl	164-6
33	3-Cl-phenyl	H	152-4
34	2-Me-phenyl	H	101-2
35	1-naphthyl	H	94-6
36	2-CF ₃ -phenyl	H	161.5-3

Example 5

A mixture of the Compound 1a (2g) and acetic anhydride (50 ml) was heated under
 5 reflux for 2 hours, after which it was poured into water, stirred for 1 hour, and
 extracted into ethyl acetate. The extract was washed and dried over magnesium
 sulfate. Removal of the solvent gave a brown solid which was recrystallised from
 acetonitrile to give 6-methoxy-2'-(5-methyl-1,2,4-oxadiazol-3-yl)nicotinamide,
 m.p. 125-6° C. (Compound 50)

In a similar manner, the following compounds of formula I were obtained:

Compound	W	R	m.p.(° C)
51	Cl	Me	147-9
52	H	Et	123-5
53	Cl	Pr ⁱ	133-5
54	H	CF ₃	125-7

Example 6

- 5 To a solution of Compound 50 (0.5 g) in hot ethanol (20 ml) was added with stirring a solution of copper (II) chloride (0.11 g) in water (0.5 ml). The mixture was allowed to cool to room temperature and then stirred overnight. The solid was collected by filtration, washed with ethanol, water and acetone and dried *in vacuo* to give bis-[6-methoxy-2'-(5-methyl-1,2,4-oxadiazol-3-yl)nicotinamide]
- 10 copper(II)chloride complex, m.p. 213-4° C (dec.) (compound 60).

Test Example

Compounds are assessed for activity against one or more of the following:

- Plasmopara viticola*: vine downy mildew
- Erysiphe graminis f. sp. hordei*: barley powdery mildew
- 5 *Erysiphe graminis f. sp. tritici*: wheat powdery mildew
- Pyricularia oryzae*: rice blast
- Pellicularia sasakii*: rice sheath blight
- Botrytis cinerea*: grey mould
- Venturia inaequalis*: apple scab
- 10 *Leptosphaeria nodorum*: glume blotch

- Aqueous solutions or dispersions of the compounds at the desired concentration, including a wetting agent, were applied by spray or by drenching the stem base of the test plants, as appropriate. Plants or plant parts were then inoculated with appropriate test pathogens and kept under controlled environment conditions suitable for maintaining plant growth and development of the disease. After an appropriate time, the degree of infection of the affected part of the plant was visually estimated. Compounds are assessed on a score of 1 to 3 where 1 is little or no control, 2 is moderate control and 3 is good to total control. At a concentration of 500 ppm (w/v) or less, the following compounds scored 2 or more against the fungi specified

- Plasmopara viticola*
17, 18, 61
- Erysiphe graminis f. sp. hordei*
25 1a, 50-52
- Erysiphe graminis f. sp. tritici*
1b, 2, 5, 9-14, 26, 50-54, 61
- Pyricularia oryzae*
18, 19
- 30 *Pellicularia sasakii*
7
- Botrytis cinerea*
5, 23, 24, 26

Venturia inaequalis

1a

Leptosphaeria nodorum

17

5

Comparison Test Example

Compounds of Examples 1 and 6-methoxy-2'-(5-methyl-1,3,4-thiadiazol-2-yl)nicotinilide (compound X) which is the prior art compound of closest structure were assessed for activity against the following:

10 *Erysiphe graminis tritici*: wheat powdery mildew

Erysiphe graminis hordei: barley powdery mildew.

The compounds were tested as previously but at more rates and with more replicates.

Results obtained were as follows: (a blank means the compound was not tested at that rate)

15

Erysiphe graminis tritici

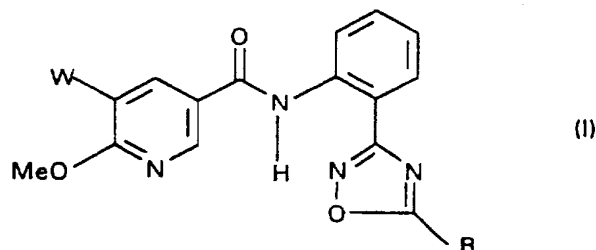
Rate (g/ha)	% Control	
	Compound 50	Compound X
80	100	86
10	99	82
0.63	90	NT

Erysiphe graminis hordei

Rate (g/ha)	% Control	
	Compound 50	Compound X
80	100	83
20	96	11
1.25	87	NT

CLAIMS

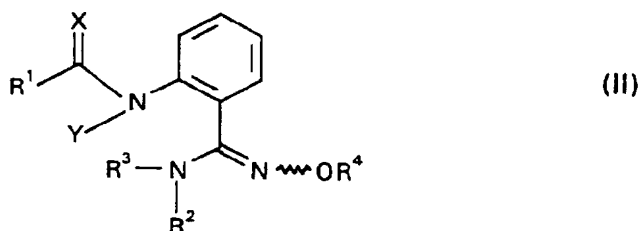
1. Compounds of formula I:



- 5 where W is H or halogen, and R is alkyl or trifluoromethyl, and complexes thereof.

2. 6-Methoxy-2'-(5-methyl-1,2,4-oxadiazol-3-yl)nicotinamide and complexes thereof.

- 10 3. Compounds of formula II



where

X is O or S;

- 15 Y is alkyl, cycloalkyl, cycloalkenyl, alkenyl or alkynyl, each of which is optionally substituted, hydrogen or acyl;

R¹ is a phenyl or a 5 or 6 membered heterocyclyl group, each of which is optionally substituted

- 20 R² and R³ are hydrogen or alkyl or together with the nitrogen to which they are attached can form an optionally substituted ring which can contain 0 to 3 extra hetero atoms selected from nitrogen, oxygen or sulfur; and

R⁴ is hydrogen or acyl;

together with complexes with metal salts, as well as salts with bases of compounds which are acids and salts with acids of compounds which are bases,

- 25 4. A fungicidal composition which comprises a compound according to claim 1 or 2 or a complex thereof in association with agriculturally acceptable diluents.

- 5 The use as a phytopathogenic fungicide of a compound according to any one of claims 1 to 3

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 97/00388

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07D413/12 C07D213/82 C07C259/18 C07D307/68 C07D317/68
C07D333/70 A01N43/40 A01N37/52 A01N43/08 A01N43/30
A01N43/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07D C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMICAL ABSTRACTS, vol. 115, no. 7, 19 August 1991 Columbus, Ohio, US; abstract no. 71523b, D. KORBONITS ET AL.: "Recent results on the cyclization tendency of diacyl-2-aminobenzamidoximes" page 789; XP002030849 see abstract & ACTA CHIM. HUNG., vol. 127, no. 6, 1990, pages 795-802, --- -/--	3,4

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

13 May 1997

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 97/00388

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMISCHE BERICHTE, vol. 122, no. 6, June 1989, WEINHEIM DE, pages 1107-12, XP002030847 D. KORBONITS ET AL.: "Ring transformation of 1,2-disubstituted 4(1H)-quinazolone oximes to 3,5-disubstituted 1,2,4-oxadiazoles" see the whole document, particularly page 1107, compounds 8f and 8g ---	3,4
X	TETRAHEDRON LETTERS, vol. 24, no. 51, 1983, OXFORD GB, pages 5763-6, XP002030848 D. KORBONITS ET AL.: "A novel ring transformation: 1,2,4-oxadiazoles from pyrimidine-N-oxides" see the whole document, particularly compound 5 ---	3,4
Y	WO 95 25723 A (AGREVO UK LIMITED) 28 September 1995 cited in the application see the whole document, particularly examples 41, 79, 98, 114, 145 and 177 ---	1-5
Y	EP 0 276 432 A (CIBA-GEIGY AG) 3 August 1988 see the whole document ---	1-5
P,Y	WO 96 16954 A (AGREVO UK LIMITED) 6 June 1996 see the whole document, particularly example 138 ---	1-5
E	WO 97 10228 A (AGREVO UK LIMITED) 20 March 1997 see the whole document, particularly examples 3, 5 and 6, first steps -----	3,4

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/GB 97/00388

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WO 9710228 A	20-03-97	NONE	